

Environmental effects on electron spin relaxation in N@C₆₀

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We examine environmental effects of surrounding nuclear spins on the electron spin relaxation of the N@C₆₀ molecule (which consists of a nitrogen atom at the centre of a fullerene cage). Using dilute solutions of N@C₆₀ in regular and deuterated toluene, we observe and model the effect of translational diffusion of nuclear spins of the solvent molecules on the N@C₆₀ electron spin relaxation times. We also study spin relaxation in frozen solutions of N@C₆₀ in CS₂, to which small quantities of a glassing agent, S₂Cl₂ are added. At low temperatures, spin relaxation is caused by spectral diffusion of surrounding nuclear ^{35,37}Cl spins in the S₂Cl₂, but nevertheless, at 20 K, T₂ times as long as 0.23 ms are observed.

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I. INTRODUCTION

The N@C₆₀ molecule has been known to contain a remarkably well-shielded electron spin [1], prompting several proposals for fullerene-based quantum information processing (QIP) [2, 3]. Electron spin relaxation in N@C₆₀ was recently studied in detail in a CS₂ solvent environment (in which there are no naturally abundant nuclear spins), and found to be primarily limited by a vibrational spin-orbit Orbach mechanism [4]. However, this solvent is not appropriate for temperatures below 160 K: CS₂ freezes as a polycrystal, leaving regions of high fullerene concentration around grain boundaries. This dramatically increases the local spin concentration, and T₂ becomes extremely short due to dipolar spin coupling (the so-called instantaneous diffusion effect [5, 6, 7]). For low temperature work, it is therefore necessary to either use a solvent which freezes as a glass (such as toluene), or to add a glassing agent such as S₂Cl₂ (sulphur chloride) to the primary CS₂ solvent. Both options necessarily involve introducing a significant nuclear spin concentration to the N@C₆₀ environment, leading to further potential relaxation pathways.

In this paper, we extend the studies of electron spin relaxation of N@C₆₀ to lower temperatures, using a range of different solvent environments. We show how the presence of nuclear spins in the surrounding environment can shorten the relaxation time. Depending on the temperature regime being studied, translation or spectral diffusion of nuclear spins surrounding the N@C₆₀ molecule will contribute to electron spin relaxation.

II. MATERIALS AND METHODS

The aggregation (or clustering) of C₆₀ in certain solvents and concentrations has been widely reported [8, 9, 10, 11, 12, 13, 14]. Furthermore, the solubilities of C₆₀ in toluene and in CS₂ show a strong temperature dependence, peaking at 280 K and falling rapidly upon further cooling [15]. The result is that the convenient picture of isolated fullerenes in solution is rather naïve, being instead a complex, non-monotonic function of temperature, fullerene concentration, choice of solvent, and even time from initial dissolution. For example, in CS₂ at room temperature the onset of aggregation has been measured to be around 0.06 mg/ml [8]. At concentrations above 0.36 mg/ml, the clusters themselves further agglomerate to form ‘flowerlike’ structures with an open hole in the centre. In toluene, clusters ranging from 3 to 55 fullerenes have been observed over a dilute range of concentrations (0.18 to 0.78 mg/ml) [14]. This clustering can have important consequences on electron spin relaxation rates resulting in a distribution of the relaxation times depending on the location of N@C₆₀ within the cluster. An additional complication can arise in samples of higher N@C₆₀/C₆₀ purity - if the large C₆₀ cluster contains two N@C₆₀ molecules within then their relaxation will be strongly affected by the dipole-dipole interaction between two N@C₆₀ electron spins. For example, on a sample of 3% N@C₆₀/C₆₀ purity, we have observed a decrease in T₂ with increasing fullerene concentration above about 0.1 mg/ml.

To eliminate uncertainties of C₆₀ cluster formation, the diluted solutions with concentrations less than 0.06 mg/ml were used in this study. High-purity (≈ 80%) endohedral N@C₆₀ were used to prepare samples in toluene, enabling the use of dilute solutions 2 μg/ml of well-isolated fullerenes which nevertheless provide sufficient signal for pulsed EPR experiments. Solutions were degassed by freeze-pumping in three cycles to remove paramagnetic O₂. We observe that while samples

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of N@C_{60} in CS_2 are stable, the EPR signal from the sample in degassed toluene decayed when exposed to the light. The precise nature of this decay is unknown and possibly occurs via the photo-excited triplet state of the C_{60} cage leading to escape of the nitrogen from the cage. Other experimental parameters, including a brief description of the N@C_{60} spin system are provided elsewhere [4]. T2 and T1 times were obtained using Hahn echo and inversion recovery sequences, respectively.

Given the strong reactivity of S_2Cl_2 , there was some concern that it might attack the fullerenes in the solution — this dictated the sample preparation procedure adopted. 50 μl samples of N@C_{60} (4% purity) in CS_2 , and pure S_2Cl_2 were degassed in two separate arms of the λ -shaped quartz vessel. The solvents were then mixed and quickly frozen; the resulting mixture contained approximately 25% S_2Cl_2 by volume (corresponding to 20 mol%).

III. SPIN RELAXATION OF N@C_{60} IN TOLUENE SOLUTIONS

When N@C_{60} is dissolved in a solution containing nuclear spins (such as the hydrogen atoms of toluene), additional relaxation pathways may be introduced. These arise from fluctuating fields caused by the motion of solvent molecules around the fullerene cage. The use of both regular (hydrogenated) and deuterated toluene as solvents can provide further insights into the effect of local nuclear spins. Figures 1 and 2 show the T_1 and T_2 times measured for high-purity N@C_{60} in toluene solution, as a function of temperature.

The temperature dependence of T_1 in toluene is suggestive of an Orbach relaxation mechanism, similar to reported for N@C_{60} in CS_2 [4]. However, the slopes of the temperature dependence are markedly different in two solvents. In CS_2 the energy splitting derived from the slope matched well the first excited $H_g(1)$ vibrational mode of C_{60} at 33 meV, and in toluene the slope corresponds to an energy splitting of 60(2) meV which coincides with the second major line seen in the Raman spectra (61 meV), corresponding to the $A_g(1)$ mode (Figure 1B). Solvent effects have been reported extensively in the Raman spectroscopy of C_{60} [?], and it is concluded that the nature of the solvent-fullerene interaction can distort the icosahedral symmetry leading to splittings of the H_g Raman transitions [?]. Consistently, the results here can also be attributed to interactions between the cage and the solvent (e.g. a π -stacking arrangement in the case of the aromatic toluene molecule), the transitions involving the $H_g(1)$ mode may be suppressed, and electron spin relaxation of the endohedral nitrogen takes places more effectively via the higher-energy $A_g(1)$ squeezing mode.

The T_2 relaxation data in Figure 2 reveal a non-monotonic temperature dependence in contrast to that observed for N@C_{60} in CS_2 [4]. In CS_2 , the simple ra-

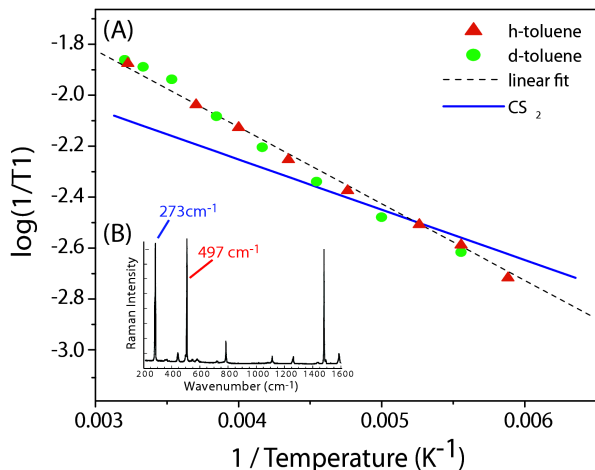


FIG. 1: (A) Spin relaxation time T_1 for N@C_{60} in toluene as a function of temperature, plotted as $\log(1/T_1)$ against $(1/T)$, where T_1 is given in microseconds. T_1 times are indistinguishable for both regular toluene (red triangles) and deuterated toluene (green circles). The linear fit (dashed line) is consistent with an Orbach relaxation mechanism, and the slope to the fit gives an energy splitting $\Delta = 60(2)$ meV of the excited state involved in the relaxation process. Similar linear dependence has been reported for N@C_{60} in CS_2 [4], but the linear fit (shown in blue, for comparison) gave a different $\Delta = 33$ meV. (B) Two major absorption peaks in the Raman spectrum of C_{60} lies at 273 and 497 cm^{-1} (33 and 62 meV, respectively).

tio of $T_2 = 2/3 T_1$ was found in the broad temperature range indicating that both T_1 and T_2 times are determined by the same Orbach relaxation mechanism. In toluene, T_2 diverges noticeably from the T_1 dependence indicating that additional relaxation mechanism must be involved which suppresses T_2 at low temperatures. In the following discussion we argue that this additional relaxation mechanism is due to nuclei spins (protons) of the toluene solvent.

In liquid solutions, solvent molecules can diffuse around N@C_{60} and therefore the distance between the electron spin of N@C_{60} and the nuclear spins of toluene molecules changes in time. This results in fluctuating hyperfine (contact and dipolar) fields seen by the electron spin and can produce its relaxation. In the hard-sphere approximation, the spin-spin separation varies between a value called the *distance of closest approach* (d), and infinity. The translation diffusion time, τ_D , becomes the important correlation time [16]:

$$\tau_D = \frac{2d^2}{D(T)}, \quad (1)$$

where $D(T) = D_{\text{C}_{60}}(T) + D_{\text{tol}}(T)$ is the sum of the temperature-dependent diffusion coefficients of the fullerene and toluene molecules. According to common models for diffusion-induced spin relaxation [17, 18, 19], the resulting T_1 and T_2 times are as follows [16]:

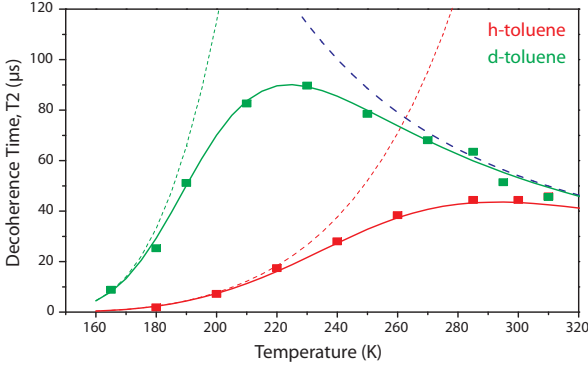


FIG. 2: Spin decoherence time T_2 of $N@C_{60}$ in toluene, measured using the central $M_I = 0$ line, with regular toluene (red squares) and deuterated toluene (green squares). The solid curves are generated using the model that involves two relaxation mechanisms, and the dashed curves show individual contributions of the two mechanisms. The blue dashed curve is the ‘intrinsic’ decoherence time due to Orbach relaxation process; $T_2 = (2/3)T_1$ is assumed based on the study of $N@C_{60}$ in CS_2 [4]. The red and green dashed curves show the relaxation effect due to translational diffusion of proton and deuterium nuclei of toluene molecules.

$$(T_1)^{-1} = 2\kappa \frac{c(T)}{d \cdot D(T)} 10J(\omega_e), \quad (2)$$

$$(T_2)^{-1} = \kappa \frac{c(T)}{d \cdot D(T)} [4J(0) + 10J(\omega_e) + 6J(\omega_n)]. \quad (3)$$

ω_e and ω_n are the electron and nuclear Zeeman frequencies, respectively. The constant prefactor, κ , is given by:

$$\kappa = \frac{16\pi}{405} \gamma_e^2 \gamma_n^2 \hbar^2 I(I+1). \quad (4)$$

γ_e and γ_n are the electron and nuclear gyromagnetic ratios, $c(T)$ is the temperature-dependent concentration of hydrogen (or deuterium) spins, and the spectral density function $J(\omega)$ is given by:

$$J(\omega) = \frac{1 + 5z/8 + z^2/8}{1 + z + z^2 + z^3/6 + 4z^4/81 + z^5/81 + z^6/648}, \quad (5)$$

with $z = \sqrt{2\omega\tau_D}$.

The only unknown quantities in the above expressions are nuclear spin concentration $c(T)$, distance of closest approach d , and the diffusion coefficient $D(T)$. The temperature dependence of 1H concentration in toluene is given in Perry’s Chemical Engineer’s Handbook (7th Ed):

$$c(T) = (4.089 \cdot 10^{21}) \left(0.26655^{-\left(1 + \left(1 - \frac{T}{591.8}\right)^{0.2878}\right)} \right), \quad (6)$$

and varies between about $4.5 - 5 \cdot 10^{22} \text{ cm}^{-3}$ over the temperature range 150 – 300K. Evidently, the variation in this parameter is not great and therefore could not explain the temperature dependence of T_2 . It must be $D(T)$ and its strong temperature dependence that dominates the effect on T_2 .

The self-diffusion coefficient $D(T)$ of toluene has been studied as a function of temperature [20]. In the temperature range 135 to 330K, the data is a good fit to the following function:

$$D_{tol}(T) = 6.1 \cdot 10^{-4} \exp\left(-\frac{1000}{T}\right) \exp\left(-\left(\frac{190}{T}\right)^6\right) \quad (7)$$

The diffusion coefficient for C_{60} can be roughly estimated by the Stokes-Einstein equation:

$$D_{C_{60}}(T) = \frac{k_B T}{6\pi a \eta(T)}, \quad (8)$$

where $a = 0.35 \text{ nm}$ is the radius of the $N@C_{60}$ molecule, and $\eta(T)$ is the solvent viscosity which can also be temperature dependent. However, reports on toluene viscosity only go down to 225K [21], below which one would expect substantial changes in behaviour. As a result, both $D_{C_{60}}(T)$ and d were left as fitting parameters.

To fit the experimental data in Figure 2 we assumed two relaxation processes: the translational diffusion mechanism described above and the Orbach relaxation mechanism which if alone would produce $T_2 = (2/3) T_1$, as was found for $N@C_{60}$ in CS_2 solution [4]. The individual contribution of each of the two relaxation mechanisms and their overall effect are shown in Figure 2. The best fit was achieved using a diffusion coefficient whose temperature dependence is shown in Figure 3, and $d = 0.35 \text{ nm}$ (though it was possible to obtain reasonable fits for d up to about 0.45 nm). The radius of the C_{60} molecule is 0.35 nm, so these values for distance of closest approach are reasonable. The best-fit diffusion coefficient of C_{60} converges with that predicted by the Stokes-Einstein equation (Eq. 8) for temperatures below 250K, however it deviates by as much as a factor of 10 at higher temperatures (310K).

Finally, evaluating Eq. 2 with the parameters extracted from the study of T_2 , we confirm that the T_1 times for h-toluene and d-toluene are expected to be equal, as the translational diffusion T_1 rates are much slower than the intrinsic (Orbach) decay mechanism (see Figure 4).

IV. SPIN RELAXATION OF $N@C_{60}$ IN A FROZEN SOLUTION

A glass-forming solvent is essential for frozen solution studies of $N@C_{60}$, in order to ensure homogeneity of the frozen solution and to avoid clustering of $N@C_{60}$. The ideal solvent would also contain a minimal concentration

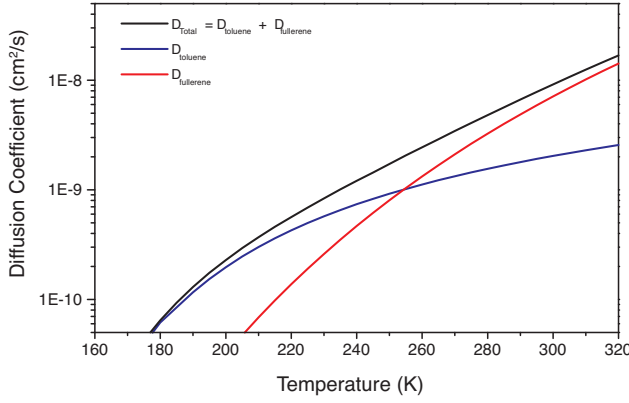


FIG. 3: Temperature dependence for (blue curve) self-diffusion coefficient of toluene, D_{tol} , based on experimental results [20]; (red curve) the predicted diffusion coefficient of C_{60} in toluene, D_{C60} , which produces the best fits to the data in Figure 2; (black curve) the overall diffusion coefficient, $D = D_{tol} + D_{C60}$.

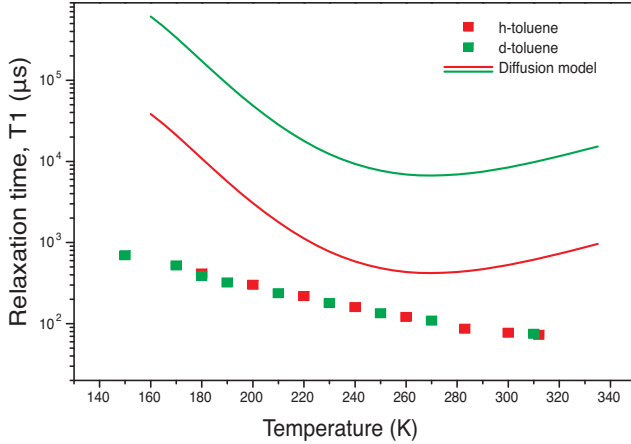


FIG. 4: (Squares) Experimental T_1 values for $N@C_{60}$ in regular (red) and deuterated (green) toluene. (Curves) Theoretical T_1 predicted from the model of relaxation by translational diffusion of nuclear spins in the solvent molecules (Eq. 2).

of nuclear spins since it is known that nuclear spins of the solvent molecules can provide significant mechanism for electron spin decoherence, e.g. via the process known as "spectral diffusion" caused by flip-flops of the local nuclear spins [5, 22, 23]. While such an ideal solvent has not come to our attention, it is possible to add relatively small quantities of sulphur chloride (S_2Cl_2) to CS_2 to act as a glassing agent [24]. The addition of 15 mol% S_2Cl_2 in CS_2 is sufficient to permit vitrification of small samples. CS_2 has no major isotopes with non-zero nuclear spins, however, S_2Cl_2 has chlorine whose both major isotopes have nuclear spin $I = 3/2$ and gyromagnetic ratios of about 4 MHz/T. Therefore, while this mixture is not an optimal solution, it was hoped that the reduced nuclear spin concentration in the mixture solution would permit relatively long decoherence times, not limited by the nu-

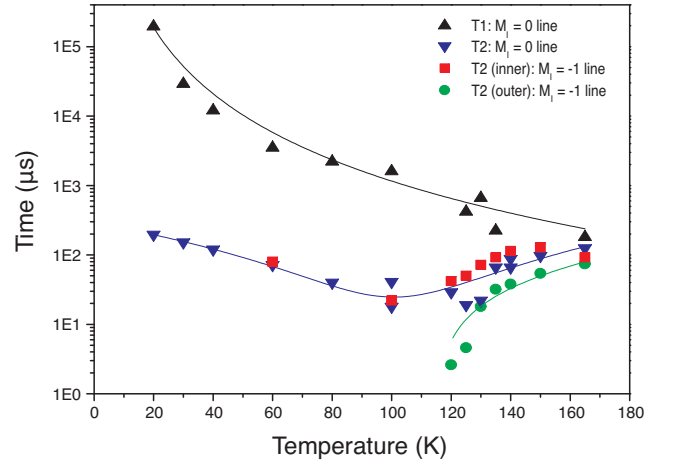


FIG. 5: Temperature dependence of T_1 and T_2 times for $N@C_{60}$ in a frozen solution of $CS_2 : S_2Cl_2$ (volume 3:1), measured on the central ($M_I = 0$) and high-field ($M_I = -1$) hyperfine lines of the $N@C_{60}$ EPR spectrum. For $M_I = -1$, two T_2 times, T_{2o} and T_{2i} , are extracted for outer ($M_S = \pm 3/2 : \pm 1/2$) and inner ($M_S = +1/2 : -1/2$) transitions within the $S=3/2$ multiplet, using their different ESEEM frequencies [4]. The curves are visual guides.

clear spectral diffusion.

The T_1 and T_2 times measured on the central ($M_I = 0$) and high-field ($M_I = -1$) hyperfine lines are shown in Figure 5, in the temperature range 20 to 165K (below the melting point of the mixture). Starting with the data obtained at $M_I = 0$, T_1 has a monotonic temperature dependence, and follows closely that seen in a powder of $C_{60}:N@C_{60}$. T_2 shows a minimum at around 100K, which coincides with the glass transition temperature, T_g , of the solvent mixture (i.e. the point at which molecular diffusion is frozen out).

Two different T_2 times corresponding to the outer ($M_S = \pm 3/2 : \pm 1/2$) transitions and inner ($M_S = +1/2 : -1/2$) transitions can be separated using the ESEEM method described elsewhere [4]. $T_{2,o}$ (outer) falls dramatically upon cooling towards T_g . $T_{2,i}$ (inner) reaches a minimum at T_g , but then rises as the temperature is lowered further. We can now see that the T_2 measured on the central line is indeed the average of the two separate T_2 times (inner and outer), for temperatures above T_g . Below T_g , the outer coherences decay sufficiently quickly that they are not detected in the electron spin echo experiment.

The behaviour of $T_{2,o}$ may be explained by a ZFS strain throughout the sample. The glassy solvent matrix around the fullerene may impose some distortion of the cage, especially approaching T_g and below. This would introduce a permanent ZFS which varies between different $N@C_{60}$ molecules. Providing all transitions corresponding to one M_I hyperfine line are excited, such a ZFS strain would not be refocused in the spin echo experiment and appear instead as an additional decay mechanism on the outer coherences.

Molecular diffusion of nuclear spins around N@C₆₀ has already been shown to be a relaxation mechanism in toluene samples (see Section III). It is possible that it is this slow diffusion, and its freezing out, which is responsible for the dip in $T_{2,i}$ around T_g . As the temperature is decreased, $T_{2,i}$ falls initially, as described by Eq. 3. However, in the limit of slow diffusion this equation is no longer valid. Molecular motion becomes frozen out and the effect of local impurity spins is better described in terms of spectral diffusion in a solid matrix.

An important relaxation mechanism for electron spins in the solid state is spectral diffusion caused by flip-flops of local nuclear spins, as seen in phosphorous doped silicon [25]. For natural silicon, the electron spin decoherence time due to spectral diffusion from ²⁹Si is about 600 μ s. In our mixture of CS₂ and S₂Cl₂, the nuclear spin density, C_n , is about 1.5 times greater, and the product of the nuclear spin and nuclear g factor ($g_n I_n$) of chlorine nuclei is about 1.3 times greater than that for silicon. There are several different models for spectral diffusion, which match experimental data with varying degrees of success [5]. We note that these models predict higher order terms in the echo decay rate, $\exp(-(\tau/T_s)^n)$, where $2 \leq n \leq 3$, while all our data show good monoexponential fits. If we assume the contribution to decoherence via spectral diffusion, T_s , goes as

$$T_s \propto (g_n I_n)^{-11/7} C_n^{-1}, \quad (9)$$

and make a comparison with the data for natural silicon, we obtain an estimate of $T_s = 315 \mu$ s for our system. This value can only be interpreted as a ballpark figure, and as such it is entirely consistent with the data presented in

Figure 5. In particular, contact hyperfine interaction is cited as the dominant electron-nuclear spin interaction term in the silicon sample, rather than dipolar coupling. In this case, it is difficult to make an estimate of T_s simply by comparing the concentration and moment of nuclear spins.

V. CONCLUSIONS

In summary, the effect of nuclear spins in the solvent surrounding N@C₆₀ on the decoherence time has been demonstrated using two different isotopes of hydrogen. The data is well fit to a model for relaxation by translational diffusion, providing estimates of the diffusion coefficient for C₆₀ in toluene. Decoherence times approaching 0.23 ms were observed at temperatures below 20K in a mixture of CS₂ and S₂Cl₂, demonstrating this to be a good choice of solvent for low-temperature studies on N@C₆₀.

VI. ACKNOWLEDGEMENTS

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